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(54) SURFACE-SIZING AGENT FOR PAPER MAKING

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a surface-sizing agent for a paper making excellent in sizing effects by performing an emulsion polymerization of polymerizable hydrophobic monomers in an aqueous medium containing a specific cationic copolymerized compound as an emulsifying and dispersing agent.

SOLUTION: This surface-sizing agent is obtained by performing an emulsion polymerization of 30-70 wt. % styrene-based compound with polymerizable hydrophobic monomers containing 30-70 wt. % (meth)acrylic acid ester expressed by the formula: $\text{CH}_2=\text{C}(\text{R}_3)\text{COOR}_4$ (R3 is H or methyl; R4 is a 1-8C, preferably a 3-8C hydrocarbon) in an aqueous medium containing a cationic copolymer obtained by making a copolymer containing 50-95 wt. % styrene-based compound with 5-50 wt. % dialkylaminoalkyl(meth)acrylamide expressed by the formula: $\text{CH}_2=\text{C}(\text{R}_1)\text{CONANR}_2\text{R}_2$ (R1 is H or methyl; R2 is methyl or ethyl; A is a 2-6C alkylene) of a quaternary salt as an emulsifying and dispersing agent.

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 CLAIMS

[Claim(s)]

- [Claim 1] A styrene system compound (a) and general formula (1): $\text{CH}_2=\text{C}(\text{R}_1)\text{CONANR}_2$ (However, in R1, R1 a methyl group or an ethyl group for hydrogen or a methyl group) Dialkylamino alkyl (meta) acrylamide (b) displayed is made into a configuration monomer. A -- an alkylene group of carbon numbers 2-6 -- being shown -- A sizing compound for paper manufacture using what was made to carry out the emulsion polymerization of the polymerization nature hydrophobic monomer (C), and was obtained in aqueous media which contains a cation nature copolymerization compound (B) of structure where an amino group originating in the above (b) of a copolymer (A) which it comes to contain is formed into 4 class, as an emulsification dispersant.
- [Claim 2] A surface-size agent for paper manufacture according to claim 1 to which a configuration monomer of said copolymer (A) comes to contain a styrene system compound (a) 50 - 95 % of the weight, and dialkylamino alkyl (meta) acrylamide (b) five to 50% of the weight.
- [Claim 3] A surface-size agent for paper manufacture according to claim 1 or 2 to which a polymerization nature hydrophobic monomer (C) comes to contain acrylic ester (c) expressed with styrene system compound (a) and general formula (2): $\text{CH}_2=\text{C}(\text{R}_3)\text{COOR}_4$ (however, R3 shows hydrogen or a methyl group, and R4 shows a hydrocarbon group of carbon numbers 1-18) (meta).
- [Claim 4] (Meta) A surface-size agent for paper manufacture according to claim 3 whose R4 of acrylic ester (c) is the hydrocarbon group of carbon numbers 3-6.
- [Claim 5] A surface-size agent for paper manufacture according to claim 1 to 4 to which a polymerization nature hydrophobic monomer (C) comes to contain a styrene system compound (a) 30 - 70 % of the weight, and (meta) acrylic ester (c) 30 to 70% of the weight.
- [Claim 6] A surface-size agent for paper manufacture according to claim 1 to 5 whose operating rate (weight ratio) of a water-soluble cation nature copolymerization compound (B) and a polymerization nature hydrophobic monomer (C) is (B):(C) = 1:4-4: 1.

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 DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the surface-size agent for paper manufacture. Although the surface-size agent for paper manufacture of this invention is applicable to various kinds of stencil paper, such as alkaline paper and acid paper, it is useful as a surface-size agent used especially for alkaline paper.

[0002]

[Description of the Prior Art] Before, the anionic surface-size agent using aqueous solutions, such as styrene / (meta) acrylic-acid system copolymer, and styrene / maleic-acid system copolymer, as a surface-size agent of paper is known. However, when use of fixing agents, such as a sulfuric-acid band, is restricted in the paper-making system, the paper which has size effect sufficient in such an anionic surface-size agent is not obtained. In the alkaline paper which uses a calcium carbonate for a loading material especially, the size effect was inadequate.

[0003] Since the problem concerning such alkaline paper is coped with, the alkyl ketene dimer system surface-size agent is proposed. However, an alkyl ketene dimer system surface-size agent has the late standup of a size effect, and has a problem concerning the dirt of a coater.

[0004] moreover, the cation nature surface-size agent which consists of styrene / a dialkylamino alkyl (meta) acrylamide system copolymer is proposed -- **** (publication-number No. 26997 [two to] official report) -- it was not able to be said that the paper which has sufficient size effect was obtained.

[0005]

[Problem(s) to be Solved by the Invention] This invention is the surface-size agent for paper manufacture of cation nature, and aims at offering the thing excellent in the size effect.

[0006]

[Means for Solving the Problem] this invention persons acquired the new knowledge that what was obtained by carrying out the emulsion polymerization of the polymerization nature hydrophobic monomer in aqueous media which uses as an emulsification dispersant a cation nature copolymerization compound which consists of styrene / a dialkylamino alkyl (meta) acrylamide system copolymer could give a size effect excellent in ****, as a result of inquiring wholeheartedly, in order to solve said technical problem. This invention is completed based on this knowledge.

[0007] This invention namely, a styrene system compound (a) and general formula (1): $\text{CH}_2=\text{C}(\text{R}_1)\text{CONANR}$ two R2 (However, in R1, R2 a methyl group or an ethyl group for hydrogen or a methyl group) A -- an alkylene group of carbon numbers 2-6 -- being shown -- a cation nature copolymerization compound (B) of structure where an amino group originating in the above (b) of a copolymer (A) which comes to contain dialkylamino alkyl (meta) acrylamide (b) displayed as a configuration monomer is formed into 4 class It is related with a sizing compound for paper manufacture using what was made to carry out the emulsion polymerization of the polymerization nature hydrophobic monomer (C), and was obtained in aqueous media contained as an emulsification dispersant.

[0008]

[Embodiment of the Invention] the dialkylamino alkyl (meta) acrylamide (b) as which the cation nature copolymerization compound (B) used for manufacture of the sizing compound for paper manufacture of this invention is displayed by the styrene system compound (a) and said general formula (1) -- {-- in addition, dialkylamino alkyl (meta) acrylamide means dialkylamino alkyl acrylamide and/or dialkylamino alkyl methacrylamide. The (meta) of this invention is [the following and] the same semantics. It has the structure where the amino group originating in the above (b) of the copolymer (A) obtained by copolymerizing the monomer mixture containing} is formed into 4 class. Make the 4th class-sized agent react to a copolymer (A), and it is obtained, and also this cation nature copolymerization compound (B) is obtained by copolymerizing the monomer which turned dialkylamino alkyl (meta) acrylamide (b) into the styrene system compound (a) the 4th class beforehand.

[0009] As a styrene system compound (a), styrene and/or a styrene derivative can be used, for example. As a styrene derivative, alpha methyl styrene, vinyltoluene, ethyl vinyltoluene, or KURORU methyl styrene can be illustrated.

[0010] On the other hand, as dialkylamino alkyl (meta) acrylamide (b) shown by said general formula (1), dimethylaminoethyl (meta) acrylamide, dimethylaminopropyl (meta) acrylamide, diethylaminoethyl (meta) acrylamide, diethylamino propyl (meta) acrylamide, etc. can be illustrated.

[0011] Among a copolymer (A), about 50 - 95 % of the weight is desirable still more desirable, and the operating rates of said styrene system compound (a) are 60 % of the weight or more and 90 % of the weight or less. Moreover, about 5 - 50 % of the weight is desirable still more desirable, and the operating rate of said dialkylamino alkyl (meta) acrylamide (b) is made into 10 % of the weight or more and 40 % of the weight or less. When the operating rate of a styrene system compound (a) exceeds 95% of the weight and it does not fill it to 50% of the weight from the point of emulsification dispersibility, it is not desirable from the point of a size effect. In addition, in the monomer mixture for manufacturing a copolymer (A), it is the range which does not spoil the purpose of this invention other than said styrene system compound (a) and (meta) acrylic-acid dialkylamino alkyl ester (b), and it is also possible to use together the monomer which has these and copolymerization nature.

[0012] Copolymerization of a styrene system compound (a) and the monomer mixture containing dialkylamino alkyl (meta) acrylamide (b)

can be performed with various polymerization methods to the bottom of existence of a suitable polymerization initiator. As a polymerization method, especially limitation is not carried out but can adopt various methods, such as bulk polymerization and solution polymerization, suitably. In the case of solution polymerization, alcohols, such as low-grade ketones, such as aromatic hydrocarbon, such as benzene and toluene, an acetone, and a methyl ethyl ketone, n-propyl alcohol, and iso-propyl alcohol, etc. can be used as a solvent. Especially a limit cannot be carried out about the class of polymerization initiator, either, for example, both organic peroxide, such as azo compounds, such as 2,2'-azobis isobutyronitrile, 2, and 2'-azobis -2 and 4-methyl valeronitrile, and a benzoyl peroxide, cumene hydro peroxide, tert-butyl hydro peroxide, dicumyl peroxide, and lauryl peroxide, and other redox catalyst systems can be adopted. Moreover, on the occasion of a polymerization, chain transfer agents, such as an alpha-methyl-styrene dimer, mercaptans, and secondary alcohol, can also be used. Polymerization temperature is made into about 70-140 degrees C, and reaction time is usually made into about 1 - 10 hours.

[0013] In this way, various kinds of things generally used as the 4th class-sized agent made to react to the obtained copolymer (A) can be used. If a typical thing is raised, a dimethyl sulfate, methyl chloride, an allyl chloride, ethylene chlorohydrine, benzyl chloride, or epichlorohydrin will be raised. The reaction by the 4th class-sized agent can be performed according to the method of well-known common use. A cation nature copolymerization compound (B) is obtained by the 4th class-ization of a copolymer (A). Said general formula (1) and equivalent degree of the operating rate of the 4th class-sized agent are desirable.

[0014] In addition, also when carrying out cation nature copolymerization compound (B) manufacture by copolymerizing the monomer which formed beforehand a styrene system compound (a) and dialkylamino alkyl (meta) acrylamide (b) into 4 class, the same method as a copolymer (A) can be adopted. As for the amount of the styrene system compound (a) used, it is desirable to suppose that it is the same as that of said range, and the same 4th class-sized agent of the as the above can be used for the 4th class-ization of dialkylamino alkyl (meta) acrylamide (b).

[0015] The sizing compound for paper manufacture of this invention is obtained by carrying out the emulsion polymerization of the polymerization nature hydrophobic monomer (C) in aqueous data medium which contains said cation nature copolymerization compound (B) as an emulsification dispersant. As a polymerization nature hydrophobic monomer (C), said styrene system compound (a), General-formula (2): $\text{CH}_2=\text{C}(\text{R}_3)\text{COOR}_4$ (however, R3 hydrogen or a methyl group) R4 -- the hydrocarbon group of carbon numbers 1-18 -- being shown -- the acrylic ester (c) expressed (meta) -- Furthermore (meta) -- the ester of vinyl ester, such as hydroxy group content (meta) acrylic ester, such as acrylic-acid 2-hydroxyethyl, and vinyl acetate, acrylonitrile (meta), a maleic acid, or a fumaric acid is raised.

[0016] Although a these polymerization nature hydrophobic monomer (C) can use one sort, combining it independently suitably two or more sorts, its thing containing the acrylic ester (c) expressed with a styrene system compound (a) and a general formula (2) as a polymerization nature hydrophobic monomer (C) (meta) is desirable at the point of excelling in a size effect. It is desirable at the point of excelling in a using [R4]-thing of hydrocarbon group of carbon numbers 3-6 size effect also in the acrylic ester (c) expressed especially with a general formula (2) (meta). As an example of this hydrocarbon group, n-propyl group, an isopropyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, a pentyl radical, a hexyl group, a cyclohexyl radical, benzyl, etc. can be illustrated, for example. Furthermore, it is excellent in the size effect to use the acrylic ester (c) which has the hydrocarbon group of branching structure (meta) also in the hydrocarbon group of these carbon numbers 3-6.

[0017] When a polymerization nature hydrophobic monomer (C) contains the acrylic ester (c) expressed with a styrene system compound (a) and a general formula (2) (meta), about 30 - 70 % of the weight is desirable still more desirable, and the operating rate of a styrene system compound (a) is made into 40 % of the weight or more and 60 % of the weight or less. Moreover, the operating rate of acrylic ester (meta) (c) is preferably made into 40 % of the weight or more and 60 % of the weight or less about 30 to 70% of the weight. The operating rate of this amount of polymerization nature hydrophobic single (C) is determined that sufficient size effect is acquired. In addition, as an amount of polymerization nature hydrophobic single (C), when using a styrene system compound (a) and (meta) acrylic ester (c) by the above-mentioned presentation ratio, as for other monomers, it is desirable to consider as 10 or less % of the weight in the amount of polymerization nature hydrophobic single (C).

[0018] As for a water-soluble cation nature copolymerization compound (B) and the operating rate (weight ratio) of a polymerization nature hydrophobic monomer (C), (B): (C) is usually preferably set to 1:3-3:1 1:4 to about 4:1. The operating rate concerned is determined as emulsification dispersibility with a water-soluble cation nature copolymerization compound (B) in consideration of the balance of a size effect.

[0019] A polymerization nature hydrophobic monomer (C) can be easily manufactured by carrying out an emulsion polymerization to the bottom of existence of a suitable polymerization initiator in aqueous data medium by which a cation nature copolymerization compound (B) exists. There is especially no limit also about the class of polymerization initiator, for example, both persulfate and water-soluble azo compounds, such as potassium persulfate and ammonium persulfate, and other redox catalyst systems can be adopted. Moreover, on the occasion of a polymerization, chain transfer agents, such as an alpha-methyl-styrene dimer, mercaptans, and secondary alcohol, can also be used. Polymerization temperature is made into about 70-100 degrees C, and reaction time is usually made into about 1 - 10 hours.

[0020] In this way, the surface-size agent for paper manufacture of obtained this invention is applied to various stencil paper as a surface-size agent. Especially a limit especially is not carried out for stencil paper, and it is hardly influenced by pulp, a loading material, the inner ** sizing compound, pH at the time of paper making, the paper reinforcing agent, a retention aid, etc. For example, stencil paper, such as paper-of-fine-quality stencil paper which carried out inner ** size of the paper-of-fine-quality stencil paper by which paper making was carried out under acid conditions and coat paper stencil paper, an alkyl ketene dimer, or the alkenyl succinic anhydride and by which neutral paper making was carried out and coat paper stencil paper, and a liner, is raised. Moreover, it can be used suitably also for the stencil paper containing a recovery waste paper.

[0021] The surface-size agent for paper manufacture of this invention can also be used together with an oxidized starch, a carboxymethyl cellulose, acrylamide system polymer, polyvinyl alcohol, etc. not to mention the ability to use it independently.

[0022] Moreover, the surface-size agent for paper manufacture of this invention is conventionally applied to various kinds of above-mentioned stencil paper by the well-known method of application, for example, an impregnation method, the size press method, the calender method, and the spray method. the coverage -- usually -- 0.001 - 5 g/m² (solid content) -- it is 0.005 - 1 g/m² preferably.

[0023] [Effect of the Invention] According to this invention, the surface-size agent for paper manufacture excellent in the size effect can be offered. Moreover, the dispersibility to water is good, and since there is moreover little foaming, application to the system is easy.

[0024] [Example] Although an example and the example of a comparison are given and this invention is explained concretely hereafter, this

invention is not limited to each [these] example. In addition, among each example, the section and % are weight criteria altogether, unless it mentions specially.

[0025] The (Styrene a) 70 section, the dimethylaminopropyl (acrylamide b) 30 section, the isopropyl alcohol 42.9 section, and the 2,2'-azobis isobutyronitrile 2.5 section were taught to the flask equipped with example 1 agitator, the cooling pipe, the dropping funnel, the nitrogen installation pipe, and the thermometer, and the temperature up was carried out at 80-85 degrees C for 5 hours, stirring under a nitrogen air current. Subsequently, the acetic-acid 11.5 section and the water 300 section were added. After having added the epichlorohydrin 17.8 section to the obtained copolymer (A) the appropriate back, forming the copolymer (A) into 4 class and considering as a cation nature copolymerization compound (B), the water of the specified quantity was added further and solid content was adjusted to 20%. After cooling to a room temperature, the (Styrene a) 50 section, the isobutyl (acrylate c) 50 section, and the water 350 section were added as a polymerization nature hydrophobic monomer (C), the 2 and 2'-azobis-2-amidinopropane-hydrochloride 2.5 section was added, and the polymerization reaction was performed with the reaction temperature of 70 degrees C for 5 hours. The appropriate back, the water of the specified quantity was added and solid content was adjusted to 20%. This was made into the surface-size agent for paper manufacture of this invention. The appearance of this thing was a nebula solution and the nonvolatile matter was [the viscosity of pH of 4.1 or 25 degrees C] 8cps 20.5%.

[0026] In examples 2-12 and one to example of comparison 3 example 1, the class or the amount of the class of the amount of the styrene (a) used for composition of a copolymer (A) and dialkylamino alkyl ester (meta) acrylamide (b), the amount used, or the polymerization nature hydrophobic monomer (C) used was changed as shown in a table 1, and also it reacted like the example 1, and various kinds of surface-size agents for paper manufacture were obtained. The appearance of the obtained surface-size agent for paper manufacture, a nonvolatile matter, pH, and the viscosity of 25 degrees C are shown in a table 2.

[0027] After carrying out surface sizing of various kinds of surface-size agents for paper manufacture obtained above, the performance evaluation of a size effect was performed in neutral stencil paper. An evaluation result is shown in a table 3.

[0028] (Alkaline paper)

the basis weight of 81g/m², and the Stockigt 0 second -- inner -- 0.4% of 20% [of ***** (rate of pair pulp addition); calcium carbonates], 0.05% [of alkenyl succinic-anhydride system sizing compounds] (product [made from Arakawa Chemical industry], trade name "size pineapple SA 850"), and sulfuric-acid band 0.5%, and cation-ized starch, and an anion system yield agent (the product made from Arakawa Chemical industry, trade name "kW-504") -- 0.01% [0029] (Surface sizing) equipment: -- lab size press surface-size agent: -- mixed use of oxidized starch (2.8g of solid content coverage/ m²) and the surface-size agent for paper manufacture of this invention (solid content coverage is indicated to a table 3) was carried out.

Desiccation conditions: Rotation mold auto dryer 110 degree-Cx 1 minute [0030] (Quality of paper evaluation)

Whenever [clearance Homo sapiens size]: JIS It is based on P-8122.

[0031]

[A table 1]

表面サイズ剤の組成						
カチオン性乳分化分散重合体 (重合性疎水性単量体 (C) B)						
	(a) :		(b)		(c)	
	スチレン (部)	種類	種類	(部)	スチレン (部)	種類 (部)
実施例 1	70	DMA PAA	30	50	IBA	50
実施例 2	70	DMA PAA	30	40	IBA	60
実施例 3	70	DMA PAA	30	60	IBA	40
実施例 4	85	DMA PAA	15	50	IBA	50
実施例 5	60	DMA PAA	40	50	IBA	50
実施例 6	35	DMA PAA	15	75	IBA	75
実施例 7	105	DMA PAA	45	25	IBA	25
実施例 8	70	DMA PAA	30	50	NPA	50
実施例 9	70	DMA PAA	30	50	BA	50
実施例 10	70	DMA PAA	30	50	2EHA	50
実施例 11	70	DMA PAA	30	50	LA	50
実施例 12	70	DMA PMA	30	50	IBA	50
実施例 13	70	DEA PAA	30	50	IBA	50
比較例 1	70	DMA	30	-	-	-
比較例 2	70	DMA PAA	30	-	-	-

[0032] The inside of a table 1, DMA PAA: dimethylaminopropyl acrylamide, DMA PMA: dimethylaminopropyl methacrylamide, DEA PAA: diethylamino propyl acrylamide, DMA: dimethylaminoethyl methacrylate, IBA: isobutyl methacrylate, NPA: n-propylacrylate, BA: n-butyl acrylate, 2EHA: 2-ethylhexyl acrylate, LA: Express laurylacrylate.

[0033]

[A table 2]

	不揮発分 (%)	pH	粘度 (cps)	外観
実施例 1	20.5	4.1	8	白濁溶液
実施例 2	20.5	4.2	9	白濁溶液
実施例 3	20.5	4.0	7	白濁溶液
実施例 4	20.5	4.3	8	白濁溶液
実施例 5	20.5	4.1	9	白濁溶液
実施例 6	20.5	4.0	7	白濁溶液
実施例 7	20.5	4.3	8	白濁溶液
実施例 8	20.5	4.2	8	白濁溶液
実施例 9	20.5	4.1	8	白濁溶液
実施例 10	20.5	4.2	8	白濁溶液
実施例 11	20.5	4.0	7	白濁溶液
実施例 12	20.5	4.3	8	白濁溶液
実施例 13	20.5	4.1	7	白濁溶液
比較例 1	20.5	4.2	20	白濁溶液
比較例 2	20.5	4.3	23	白濁溶液

[0034]

[A table 3]

表面サイズ剤	塗工量 (g/m ²)	
	0.07	0.14
実施例 1	20.9	33.0
実施例 2	16.2	31.5
実施例 3	18.9	32.6
実施例 4	22.4	36.5
実施例 5	18.2	32.7
実施例 6	14.8	28.4
実施例 7	16.5	31.0
実施例 8	13.1	22.5
実施例 9	15.0	28.3
実施例 10	9.3	15.4
実施例 11	8.0	12.1
実施例 12	21.9	33.4
実施例 13	22.2	33.1
比較例 1	3.2	9.2
比較例 2	1.5	6.8

[0035] The amount of coating shows the amount of solid content of a surface-size agent among a table 3.

[Translation done.]